



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 439 625 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art.  
158(3) EPC

(21) Application number: 90912373.9

(61) Int. Cl. 5: **B29C 43/02, B29C 43/18,**  
**B29C 43/34**

(22) Date of filing: 21.08.90

(66) International application number:  
**PCT/JP90/01060**

(67) International publication number:  
**WO 91/02639 (07.03.91 91/06)**

(30) Priority: 21.08.89 JP 215434/89  
09.03.90 JP 59428/90

(43) Date of publication of application:  
07.08.91 Bulletin 91/32

(84) Designated Contracting States:  
**BE DE ES FR GB IT NL**

(71) Applicant: **SUMITOMO CHEMICAL COMPANY,**  
**LIMITED**  
5-33 Kitahama 4-chome Chuo-ku  
Osaka-shi Osaka(JP)

(72) Inventor: **HARA, Takahisa**  
2-10-1-142, Sonehigasino-cho Toyonaka-shi

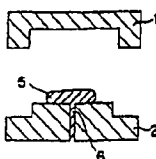
**Osaka 561(JP)**  
Inventor: **MATSUMOTO, Masahito**  
2-1-133, Kuwata-cho Ibaraki-shi  
**Osaka 567(JP)**  
Inventor: **USUI, Nobuhiro**  
1-9-1-501, Tamagawa Takatsuki-shi  
**Osaka 569(JP)**  
Inventor: **MATSUBARA, Shigeyoshi**  
1-7-3, Zulko Higashiyodogawa-ku  
Osaka-shi Osaka 533(JP)

(74) Representative: **Vossius & Partner**  
Siebertstrasse 4 P.O. Box 86 07 67  
W-8000 München 86(DE)

**(54) METHOD OF MANUFACTURING FIBER-REINFORCED THERMOPLASTIC RESIN MOLDED PRODUCT.**

(57) This invention relates to a method of manufacturing a fiber-reinforced thermoplastic resin molded product significantly small in deformation resulting from fiber orientation and excellent in appearance, luster, dimensional stability, and mechanical properties. Fiber-reinforced thermoplastic molten resin, that is, molten thermoplastic resin (A) into which fibers in length ranging from 1 to 50 mm. on the average are dispersed as a reinforcing material, is fed into an opened metallic mold on which a film or sheet comprising thermoplastic resin (A) and another adhesive thermoplastic resin (B) is mounted as required, and, with the metallic mold closed, is pressurized and cooled in a closed metallic mold to be molded into a product.

Fig. 1A



EP 0 439 625 A1

FIELD OF THE INVENTION

The present invention relates to a method for producing a molded article of a fiber-reinforced thermoplastic resin which is used as industrial materials including automobile parts such as exterior panels, structural parts and battery trays, and building materials such as access floors. More particularly, the present invention relates to a method for producing a molded article of a fiber-reinforced thermoplastic resin which is much less deformed due to orientation of the fibers and good in exterior gloss, dimensional stability and mechanical properties.

Description of the Related Art

Hitherto, some methods for producing a fiber-reinforced thermoplastic resin article have been proposed and industrially employed. One of the typical methods comprises molding the fiber-reinforced thermoplastic resin article from resin pellets which are reinforced with short-length fibers in conventional molding manners such as injection molding. Another method uses thermoplastic resin pellets which are reinforced with middle-length fibers having substantially the same length as the pellets and produces the fiber-reinforced molded article by, for example, injection molding.

However, each of the above techniques has its own technical and economical problems.

In the method using the resin pellet reinforced with the short-length fibers which is most commonly employed, improvement of the mechanical strength which is the most important object of the fiber reinforcing, particularly impact resistance is not sufficient, although moldability, design flexibility and the production cost of this technique are superior to other techniques. The reason for the insufficient increase of the mechanical strength is that, the fibers are severely broken during two plasticizing and kneading steps, namely the step for mixing and dispersing the fibers and the resins (the granulating step), and the molding step. In addition, since the fibers flow in the mold together with the resin melt in the molding step, the orientation of the fibers remains in the molded article and causes large deformation of the molded article. When the fibers, in particular, the inorganic fibers are used, they will wear screws and cylinders of extruders and an injection molding machine which are used for granulation and molding. Such wearing of the apparatuses is a big problem in view of the production cost of the molded article.

The method using the resin pellets reinforced with the middle-length fibers requires a specially designed extruder head, and the productivity is inferior to the method using the pellets reinforced with the short-length fibers. Therefore, the production cost increases. In addition, as in the case of the short-length fibers, the molded article tends to deform, and the screws and cylinders of the extruder and the injection molding machine are worn.

In addition to the above drawbacks, the molded article of the fiber-reinforced thermoplastic resin has much poorer appearance and gloss than a molded article of non-reinforced thermoplastic resin, since the fibers are exposed on the surface in the former.

SUMMARY OF THE INVENTION

As described above, since the conventional methods have respective drawbacks in mechanical properties, deformation, appearance or cost, they are not satisfactory as technical methods. The present inventors have made extensive study to develop a method which can overcome the above drawbacks, and now completed a novel method for producing a molded article of a fiber-reinforced thermoplastic resin at a low cost, which method is industrially excellent.

According to a first aspect of the present invention, there is provided (i) a method for producing a molded article of a fiber-reinforced thermoplastic resin, which comprises supplying a melt mass of a thermoplastic resin (A) which is reinforced with fibers dispersed therein and having an average fiber length of not shorter than 1 mm and not longer than 50 mm as a reinforcing material in an unclosed mold, closing the mold and pressurizing and cooling it to obtain a molded article. According to a second aspect of the present invention, there is provided (ii) a method for producing a molded article of fiber-reinforced thermoplastic resin, which comprises placing a film or sheet made of a thermoplastic resin (B) having adhesiveness to a thermoplastic resin (A) in an unclosed mold, supplying a melt mass of a thermoplastic resin (A) which is reinforced with fibers dispersed therein and having an average fiber length of not shorter than 1 mm and not longer than 50 mm as a reinforcing material in the mold, closing the mold during or after the supply of the thermoplastic resin (A) and pressurizing and cooling it to obtain a molded article.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 4 show vertical cross sections of apparatuses used in the method of the present invention,

Fig. 5 shows a cross sectional view of a plasticator for kneading a matrix resin and fibers,

Fig. 6 shows an accumulator used in Examples of the present invention,

5 Fig. 7 shows a connection of the plasticator, the accumulator and the mole used in Examples of the present invention, and

Fig. 8 is a perspective view of a box-shaped molded article produced in one embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

10

The molding methods of the present invention will be explained by making reference to the accompanying drawings.

In the first embodiment, as shown in Figs. 1 and 2, a melt mass of a fiber-reinforced thermoplastic resin is supplied in an unclosed mold, the mold is closed, pressurized and cooled to effect molding.

15 In the embodiment shown in Figs. 3 and 4, a pair of films or sheets 3, 4 made of a thermoplastic resin (B) are placed in the unclosed mold, and the mold is closed during or after supplying a fiber-reinforced thermoplastic resin comprising a thermoplastic resin (A) as a matrix material, and then the mold is pressurized and cooled to effect molding.

In the present invention, the resin melt containing fibers having a length of 1 to 50 mm which are 20 dispersed therein is supplied in an unclosed mold and then molded by a mold clamping pressure. Therefore, a pressure for supplying the resin melt in the mold is very low and from 100 to 300 kg/cm<sup>2</sup> which is much lower than a pressure of 500 to 1600 kg/cm<sup>2</sup> in case of injection molding, and the mold clamping pressure is extremely low and from 30 to 150 kg/cm<sup>2</sup>. Accordingly, the fibers dispersed in the molten matrix resin are much less broken than in the injection molding.

25 The molded article produced by the present molding method has much increased impact strength, and any part of the molded article is reinforced with long fibers.

When the film or sheet made of the thermoplastic resin (B) which has adhesiveness to the thermoplastic resin (A) is used as the outer layer in combination with the fiber-reinforced thermoplastic resin, it is possible to produce a product which is highly rigid and less deformed and has beautiful appearance of resin 30 surfaces.

In the present invention, shear should be as small as possible to prevent breakage of the fibers in the plasticizing step. To this end, for example, a plasticator as shown in Fig. 5 can be preferably used. In Fig. 5, a numeral 8 stands for a feed opening for supplying a thermoplastic resin raw material, 9 for a feed opening for supplying a fiber material, and 10 for an exhaust vent for removing gasses contained in the resin.

35 In the plasticizing step of the fiber-reinforced thermoplastic resin, the fibers are broken mainly in a first half of the plasticator, namely in a resin pellet supplying part and a compression part. Then, in the plasticator to be used in the present invention, the feed opening for supplying the fibers is provided in downstream of the compression part, namely at a part after the thermoplastic resin is well molten. Air which is entrained in the molten resin together with the supplied fibers can be effectively removed through the 40 exhaust vent which is provided between the feed opening for the fibers and a cylinder nozzle. Since the supplied fibers should be homogeneously dispersed in the resin melt, a kneading part having a length as long as possible is provided after the fibers are supplied in the resin. To this end, a ratio of screw length to screw diameter is preferably at least 15 in the present invention. By using such apparatus, it is possible to obtain the resin containing the homogeneously dispersed fibers which are long and vary seldomly broken.

45 Further, by using the above methods in which the molding is carried out using the unclosed mold, the fibers are very rarely broken, so that the molded article is uniformly reinforced by the long fibers.

As the reinforcing fiber to be used in the present invention, are used inorganic fibers such as glass fiber, carbon fiber, stainless steel fiber, etc., organic fibers such as polyamide fiber, polyester fiber, aramid fiber, etc., and mixtures thereof. When the glass fibers are used, they may be surface treated with a usual 50 organic silicon compound such as aminosilane, vinyl silane and the like. A usual fiber having a diameter of 1 to 50  $\mu$ m can be used.

In the present invention, as the fibers supplied from the feed opening for supplying the fibers which is provided in the center part of the cylinder of the plasticator, monofilament fiber having a fiber length of 1 to 50 mm, or collected fiber comprising several ten to several hundred monofilaments collected with a greige 55 agent may be used. When the fiber length is shorter than 1 mm, the mechanical strength, in particular, impact strength of the molded article is not sufficiently improved, while when the fiber length is longer than 50 mm, the fibers tends to bridge at an entrance of the feed opening for supplying the fibers so that the fibers are not smoothly supplied.

As the thermoplastic resin (A) to be used in the present invention, are used thermoplastic resins such as polyethylene, polypropylene, polystyrene, an acrylonitrile-butadiene-styrene copolymer, polyvinyl chloride, polyamide, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyphenylene ether, a styrene-acrylonitrile copolymer, and mixtures and polymer alloys thereof. In addition, there may be used a thermoplastic resin composition comprising the above thermoplastic resin and an inorganic filler such as talc, warastnite or glass fibers so as to achieve a mold shrinkage factor of 10/1000 or less and a flexural modulus of 24,000 kg/cm<sup>2</sup> or larger. The thermoplastic resin may further contain a conventional additive such as a heat stabilizer and a UV light absorber, a colorant and an elastomer.

The sheet or film of the thermoplastic resin (B) to be used in the present is formed from a thermoplastic resins such as polyethylene, polypropylene, polystyrene, an acrylonitrile-butadiene-styrene copolymer, polyvinyl chloride, polyamide, polycarbonate, polyester, polyethylene terephthalate, polybutylene terephthalate, polyphenylene ether, and mixtures and polymer alloys thereof.

#### Examples

The present invention will be illustrated by the following Examples which do not limit the scope of the present invention. The test methods used in Examples are as follows:

#### Flexural test

A three-point bending test according to JIS K 6758. Test pieces are cut out from a bottom plate of a box-shaped molded article of Fig. 8 and have a thickness of 2 mm, a width of 10 mm and a length of 90 mm. The test is carried out at 23 °C.

#### Impact test (notched Izod impact test)

According to JIS K 6758, notched Izod impact test is carried out. Test pieces are cut out from a bottom plate of a box-shaped molded article of Fig. 8 and have a thickness of 2 mm, a width of 10 mm and a length of 90 mm. This test is carried out at 23 °C.

#### Average fiber length

A obtained molded article is placed on an iron plate and heated with a burner for about one hour. Then, the article is kept in an electric furnaces at 500 °C for 2 hours to remove combustible components. After cooling, fibers are sampled from arbitrary parts and lengths or 200 fibers are measured and averaged to obtain an average fiber length.

#### Fiber content

From a molded article, a sample piece of 20 mm x 20 mm is cut out, and its weight is measured before burning. Then, the combustible components are removed in the same manner as in the measurement of average fiber length and fibers are taken out. A weight of the fibers after burning is measured and a fiber content is calculated according to the following equation:

$$\text{Fiber content (\%)} = \frac{\text{Weight of sample after burning}}{\text{Weight of sample before burning}} \times 100$$

50

#### Example 1

A vertical press molding machine with a mold locking force of 100 tons was equipped with a mold having an opening for supplying a resin melt. To a manifold of the mold, the accumulator of Fig. 6 was connected, and the plasticator of Fig. 5 was connected to the accumulator. The plasticator had a full-flighted screw with a diameter of 50 mm and a ratio of screw length to screw diameter was 29. The plasticator had a feed opening 8 for supplying the matrix resin at a rear part of a cylinder, a feed opening 9 for supplying

the fibers at a center part, and an exhaust vent 10 between the feed opening 9 for supplying the fibers and the nozzle. A vacuum pump was connected to the exhaust vent 10 and used for forced ventilation. Fig. 7 shows a connected state of the apparatuses. As the mold, was used a mold which consisted of upper and lower parts and an in-mold opening or 3 mm in diameter for supplying the resin melt at a center of the lower part and was designed for molding a box-shaped article having a wall thickness of 2 mm, and sizes or 200 mm in length, 200 mm in width and 40 mm in height (see Fig. 8).

As the thermoplastic resin, a polypropylene resin Sumitomo Noblen AX 568 (manufactured by Sumitomo Chemical Co., Ltd. having a melt flow index of 65 g/10 minutes) was used and supplied through the feed opening 8 for supplying the matrix resin. As the fiber, Glass Fiber Roving PER 231-SM14 (manufactured by Nippon Glass Fiber Co., Ltd.) was supplied after cut to a length of 13 mm with a roving cutter through the feed opening 9 for supplying the fibers in an amount of 15 % by weight based on the polypropylene weight.

A fiber content and an average fiber length were measured with samples which were cut out from a part around an accumulator nozzle and an end part of the molded article. As shown in Table, the molded article contained the less broken fibers which were homogeneously dispersed therein. By carrying out a flexural test and an impact test, improvement of the mechanical strength by the fiber reinforcement was confirmed.

#### Example 2

Under the same conditions as in Example 1 but using the polypropylene resin (Sumitomo Noblen AX 568) containing 10 % by weight or a maleic acid-modified polypropylene resin and glass fibers surfaces of which were treated with vinyl silane, the molding test was done. As shown in Table, the molded article had good mechanical strength.

#### Example 3

Under the same conditions as in Example 2 but cutting the supplied fibers to a length of 25 mm, the molding test was done. As shown in Table, the molded article had good mechanical strength.

#### Example 4

A molding test was done using a vertical press molding machine with a mold locking force of 200 tons. A mold consisted of upper and lower parts and had an in-mold opening of 2 mm in diameter for supplying the resin melt at the center of the lower part, which opening was connected to a manifold. The mold use designed for molding a box-shaped article having a wall thickness of 2.0 mm, and sizes of 200 mm in length, 200 mm in width and 40 mm in height (see Fig. 8).

First, in the mold, were placed a pair of extruded sheets Flexloy (trademark) D-2000 made of PP/EPDM/Nylon 6 and each having a thickness of 300  $\mu$ m and a hole of 10 mm in diameter at a part corresponding to the resin supplying opening of the mold.

By using a plasticator which had a full-flighted screw with a diameter of 50 mm and a ratio of screw length to screw diameter of 29 and comprised a feed opening for supplying the matrix resin at a rear part of a cylinder, a feed opening for supplying the fibers at a center part and an exhaust vent between the feed opening for supplying the fibers and the nozzle, a polypropylene resin Sumitomo Noblen AX 568 having a melt flow index of 65 g/10 minutes was supplied through the feed opening for supplying the matrix resin and, as the fiber, Glass Fiber Roving PER 231-SM14 was supplied after cut to a length of 13 mm with the roving cutter through the feed opening for supplying the fibers in an amount of 30 % by weight based on the polypropylene weight. The obtained long fiber-dispersed resin melt was filled in the accumulator and then supplied between the already placed thermoplastic resin sheets through the resin-supplying opening in the mold and the hole in the sheet. Then, the mold was closed to effect molding. As shown in Table, the molded article had good appearance and mechanical strength.

#### Comparative Example 1

Under the same conditions as in Example 1 but using a 1:1 blend of a polypropylene resin filled with 30 % by weight of glass fibers (Sumitomo Noblen GHH 43 manufactured by Sumitomo Chemical Co., Ltd., average glass fiber length of 0.7 mm) and a polypropylene resin containing no glass fiber (Sumitomo Noblen Y 101 manufactured by Sumitomo Chemical Co., Ltd.) and supplying no glass fibers through the feed opening for supplying the fibers, the molding test was done. As shown in Table, the produced article

had insufficient impact strength.

Comparative Example 2

- 5 Under the same conditions as in Example 1 but supplying the glass fibers through the feed opening 8 for supplying the matrix resin, the molding test was done. As shown in Table, the produced article had insufficiently improved impact strength.

Comparative Example 3

- 10 Under the same conditions as in Example 1 but using a plasticator having a full-flighted screw with a diameter of 50 mm and a ratio of screw length to screw diameter of 10, the molding test was done. The produced article contained bubbles therein and the fibers were insufficiently split and localized.

15 Comparative Example 4

An article was molded using no sheet of thermoplastic resin (Flexloy (trademark) D-2000). Other conditions were the same as in Example 4, and the test was done. The surface property of the molded article was inferior to that of Example 4.

20

25

30

35

40

45

50

55

Table

Exam- ple No.	Matrix resin		Glass fiber		Residual av. fiber length		Glass fiber content (%)		Flexural modulus (kg/cm <sup>2</sup> )	Notched Izod impact strength (kg.cm/cm)
	Unmodi- fied- poly- propylene	Modified poly- propylene	Cut length when supplied (mm)	Surface treat- ment	Accumu- lator nozzle part (mm)	Arti- cle end (mm)	at resin supply opening	at arti- cle end		
1	AX 568 100 %	---	13	No	7.0	5.8	15.3	15.0	33,000	16
2	AX 568 90 %	Maleic acid modified PP (10 %)	13	with silane	7.1	6.1	15.2	14.9	34,000	22
3	+	+	25	+	8.5	6.2	15.1	15.2	35,000	25
4	AX 568 100 %	---	13	No	7.0	6.0	30.2	29.9	50,000	30
Com.1	GH 43 50 % Y 101 50 %	---	17	with silane	0.4	0.4	14.3	14.6	33,000	5
Com.2	AX 568 100 %	---	13	No	1.2	0.7	15.1	15.2	33,000	6

Note: 1) The glass fibers were supplied through the feed opening for supplying the matrix resin.

## Effects of the Invention

By using the fiber-reinforced molding technique of the present invention, the article is reinforced with the long fibers simultaneously with the molding, and the article which is uniformly reinforced to its ends can

be produced at a low cost. Further, by using, as the outer layer, the film or sheet made of the thermoplastic resin (B) having adhesiveness to the thermoplastic resin (A) in combination with the fiber-reinforced thermoplastic resin, it is possible to produce the product which is rigid and less deformed and has beautiful resinous surface appearance.

5

#### Claims

1. A method for producing a molded article of a fiber-reinforced thermoplastic resin, which comprises supplying a melt mass of a thermoplastic resin (A) which is reinforced with fibers dispersed therein and having an average fiber length or not shorter than 1 mm and not longer than 50 mm as a reinforcing material in an unclosed mold, closing the mold and pressurizing and cooling it to obtain a molded article.
2. A method for producing a molded article of fiber-reinforced thermoplastic resin, which comprises placing a film or sheet made of a thermoplastic resin (B) having adhesiveness to a thermoplastic resin (A) in an unclosed mold, supplying a melt mass of a thermoplastic resin (A) which is reinforced with fibers dispersed therein and having an average fiber length of not shorter than 1 mm and not longer than 50 mm as a reinforcing material in the mold, closing the mold during or after the supply of the thermoplastic resin (A) and pressurizing and cooling it to obtain a molded article.
3. The method according to claim 1 or 2, wherein a thermoplastic resin (A) having a mold shrinkage factor of 10/1000 or less and a flexural modulus of 2400 kg/cm<sup>2</sup> or larger.
4. The method according to claim 1 or 2, which uses a fiber-reinforced thermoplastic resin containing dispersed fibers having an average fiber length of from 1 mm to 50 mm, which is prepared with a plasticator having a ratio of screw length to screw diameter of at least 15 and comprising a feed opening for supplying fibers at a center of a cylinder and an exhaust vent on a nozzle side.

30

35

40

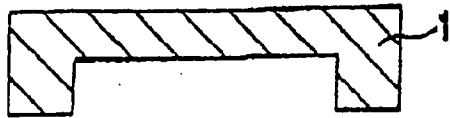
45

50

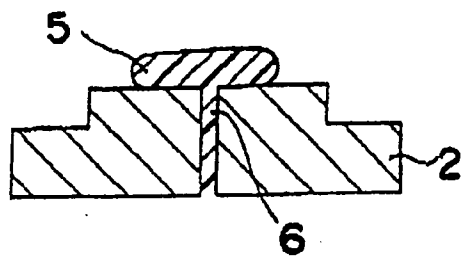
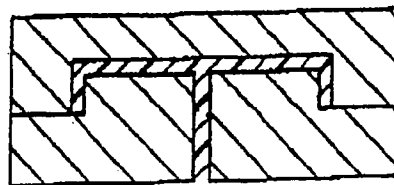
55



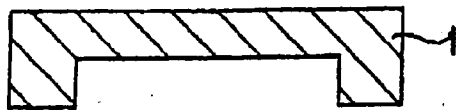
*Fig. 1A*



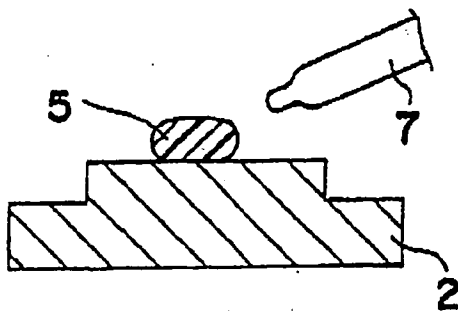
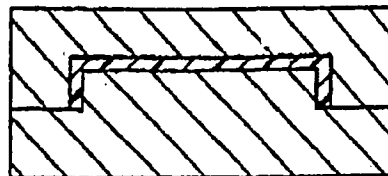
*Fig. 1B*



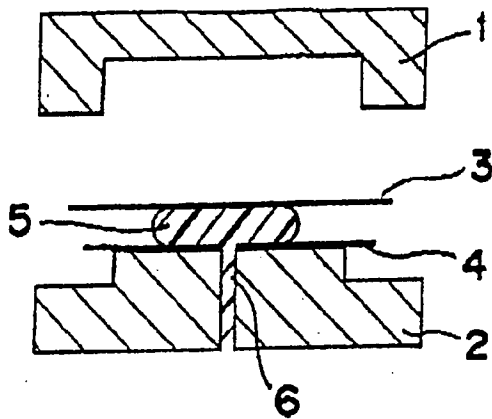
*Fig. 2A*



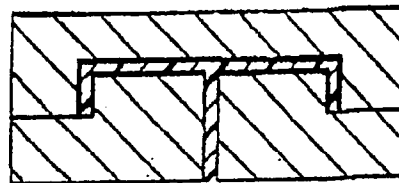
*Fig. 2B*



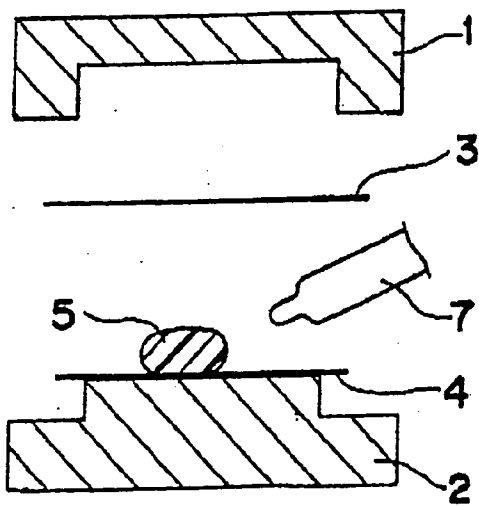
*Fig. 3A*



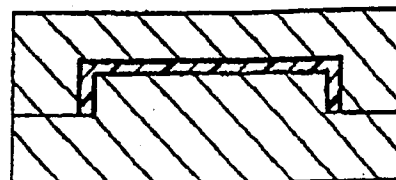
*Fig. 3B*



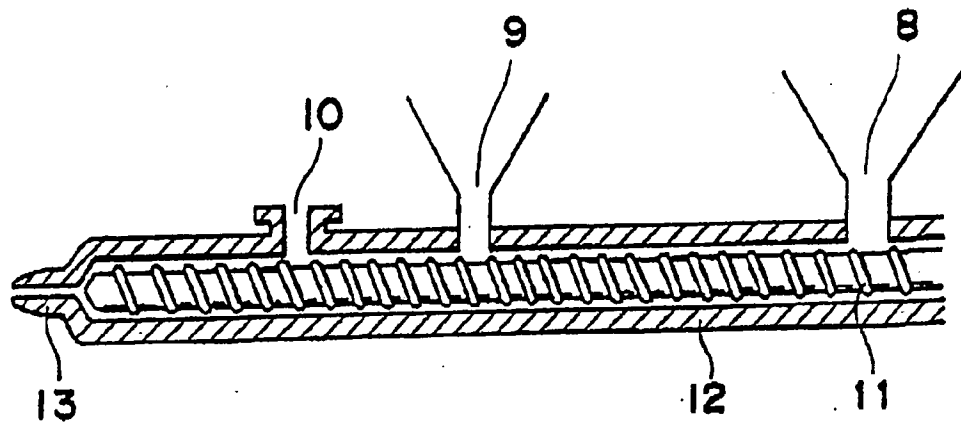
*Fig. 4A*



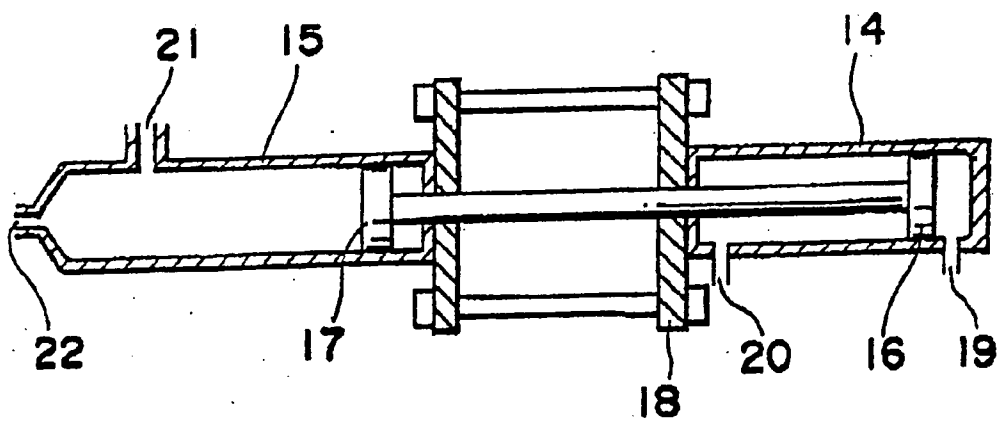
*Fig. 4B*



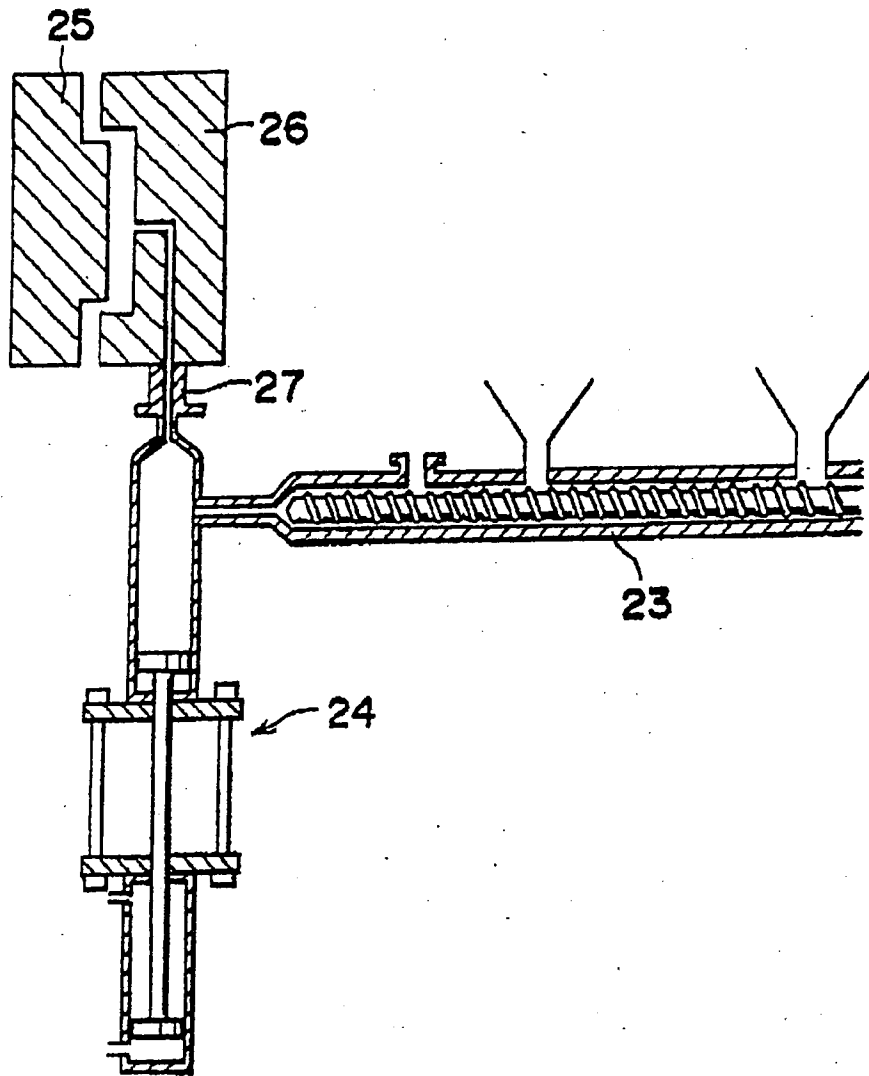
*Fig. 5*



*Fig. 6*



*Fig. 7*



*Fig. 8*

